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The Structure of 2-Amino-1,3-oxazole[*]

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Abstract. $C_3H_4N_2O$, M_r = 84·08, monoclinic, $P2_1/c$, Z = 4, a = 10·093 (4), b = 3·972 (2), c = 10·081 (4) Å, β = 78·98 (2)° (from a least-squares refinement of 2θ values of 20 reflections), V = 396·7 Å^3, D_x = 1·407 Mg m^{-3}. 714 independent reflections up to sin θ/λ = 0·5947 Å^{-1} (Mo $K\bar{\alpha}$ radiation) were collected. The structure was solved by direct methods and refined to a final R of 0·042 for 455 observed reflections. The molecule is planar and the geometry is consistent with that expected for oxazoles.

Introduction. Oxazole derivatives constitute an interesting class of substances with a wide range of applications, for example as pharmaceuticals, optical-sensitizing dyes and scintillants (for reviews see Traldi, Vettori & Clerici, 1980; Lakhan & Ternai, 1974).

Mass-spectral studies have been extensively used, beside X-ray crystallography, to determine the structure of various complex oxazoles (Traldi *et al.*, 1980). In mass-spectrometric studies, MO calculations based on various approximations have been widely used (Levsen, 1978) to describe the EI mass-spectrometric behaviour and to clarify and confirm mechanistic hypotheses; in particular simple molecules have been successfully used as model compounds.

The starting point for the calculations of the electronic distribution, both of the neutral species and the ionic moiety, is usually the X-ray-determined geometry, so accurate data on simple 'model' compounds are needed.

As part of a systematic study of some five-membered-ring heterocyclic compounds, it seemed interesting to determine and study the structure of one such 'model compound': 2-amino-1,3-oxazole. Moreover, the title compound is particularly interesting because its mass-spectrometric behaviour, which has been studied in some detail (Selva, Traldi, Rapi, Ginanneschi & Chelli, 1979), differs strongly from that of other substituted oxazoles, being influenced by the electron-donating property of the amino group.

Data were collected on an automated PW 1100 four-circle diffractometer using an $\omega/2\theta$ scan mode, up to sin θ/λ = 0·5947 Å^{-1} (graphite-monochromated Mo $K\bar{\alpha}$ radiation, λ = 0·71069 Å).

The scan speed was 0·05° s^{-1} and a constant scan width of 1·40° was used. Background was measured for 10 s at each side of the peak and the values were subsequently averaged. Out of the 714 independent reflections collected, 455 were considered as observed having $I_{\rm net} \geq 3\sigma(I)$. Three standard reflections were measured every hour to check the stability of the experimental conditions and the decay of the crystal; no significant variation was detected.

Table 1. *Final positional coordinates and temperature factors, B_{eq} or B_{iso}, with e.s.d.'s in parentheses*

$B_{\rm eq} = (B_{11} + B_{22} + B_{33})/3.$

	x	y	z	$B_{\rm eq}$, $B_{\rm iso}$ (Å^2)
C(1)	0·8099 (2)	0·8784 (6)	0·3508 (2)	2·7 (2)
C(2)	0·6174 (3)	1·1040 (7)	0·3364 (3)	3·4 (1)
C(3)	0·6987 (3)	1·1146 (8)	0·2184 (3)	3·5 (1)
N(1)	0·8243 (2)	0·9681 (5)	0·2255 (2)	3·1 (1)
N(2)	0·8982 (2)	0·7225 (7)	0·4142 (3)	4·3 (2)
O	0·6870 (2)	0·9479 (4)	0·4269 (2)	3·1 (1)
H(C2)	0·524 (3)	1·154 (8)	0·371 (3)	3·7 (7)
H(C3)	0·684 (3)	1·195 (8)	0·132 (3)	4·7 (7)
H(N2)	0·986 (3)	0·659 (8)	0·367 (3)	5·1 (7)
H′(N2)	0·874 (3)	0·705 (9)	0·500 (4)	5·2 (9)

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[*] The Structure of Substituted Oxazoles and Oxadiazoles. II. Part I. Albinati & Brückner (1978).

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Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

		Calculated*			Calculated*
C(1)–O	1·356 (3)	1·35	C(2)–C(3)	1·310 (4)	1·35
C(1)–N(1)	1·294 (3)	1·31	C(3)–N(1)	1·410 (4)	1·39
C(1)–N(2)	1·343 (4)		N–H†	0·91 (5)	
C(2)–O	1·399 (4)	1·36	C–H†	0·97 (3)	
C(1)–N(1)–C(3)	103·2 (2)	101	C(1)–N(2)–H′(N2)	116 (2)	
C(1)–O–C(2)	103·9 (2)	104	C(2)–C(3)–H(C3)	131 (1)	
O–C(1)–N(1)	114·6 (2)	115	N(1)–C(3)–H(C3)	118 (1)	
O–C(2)–C(3)	107·5 (2)	107	O–C(2)–H(C2)	116 (1)	
C(2)–C(3)–N(1)	110·7 (2)	111	C(3)–C(2)–H(C2)	136 (1)	
C(1)–N(2)–H(N2)	122 (1)				

* According to Roche *et al.* (1971).
† Average value.

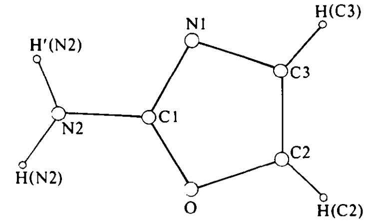

Fig. 1. A schematic view of the molecule showing numbering of the atoms.

The structure was solved with the *MULTAN* program (Main, Lessinger, Germain, Declercq & Woolfson, 1974) and refined by full-matrix least squares using a weighting scheme of the type $w = (a + |F_o| + c|F_o|^2)^{-1}$ (Cruickshank, 1970) and anisotropic thermal parameters for C, N and O atoms. H atoms were located on a difference Fourier map and subsequently refined with isotropic thermal factors. The final agreement factor was 0·042 for the observed reflections.

Scattering factors were taken from *International Tables for X-ray Crystallography* (1974). A final difference Fourier map showed no significant features. The positional and thermal parameters, bond lengths and angles are given in Tables 1 and 2 respectively. A schematic drawing of the molecule with the numbering scheme is given in Fig. 1.[*]

Discussion. The oxazole ring is planar, the maximum deviation from the least-squares plane (defined by the ring atoms) being 0·009 Å.

The bond lengths in the ring show a certain amount of shortening consistent with some aromatic character. For example the C(3)—N(1) bond length [1·410 (4) Å] is shorter than the expected value of 1·475 Å when N is sp^2 hybridized (Sutton, 1965) and comparable with the value 1·380 (5) Å found in 3-(*p*-aminophenyl)-5-phenyl-1,2,4-oxadiazole (Albinati & Brückner, 1978), or 1·403 (5) Å in 4-(*p*-chlorobenzylidene)-1,3-diphenyl-5-pyrazolone (Bovio & Locchi, 1972).

The C(1)—N(2) bond is also shorter than expected [1·343 (4) Å] and somewhat consistent with a multiple-bond character (Allman, 1975).

On the other hand the presence of two localized double bonds [C(2)—C(3) and C(1)—N(1)] is consistent with the not fully aromatic nature of the oxazole (*e.g.* facile Diels–Alder reactions, singlet oxygen auto-oxidation, *etc.*); the C(2)—C(3) bond [1·310 (4) Å] is shorter than the value of 1·351 (3) Å for a similar bond in 2-methyl-4-nitroimidazole (Kálmán, van Meurs & Toth, 1980), and 1·36 (1) Å in pyrazole (La Cour & Rasmussen, 1973), where a high degree of π delocalization is present. Another example of extensive double-bond character for the C—C and C—N bonds is found in the related compound 2,2′-*p*-phenylenebis-(5-phenyl-1,3-oxazole) (Ambats & Marsh, 1965) where values of 1·347 (4) and 1·294 (4) Å are found.

The two C—O bonds are non-equivalent, the shorter being that bonded to the carbon substituted with the electron-donating NH_2 group; both fall in the expected range for heterocyclic compounds [*e.g.* 1·371 (5) Å in furan].

The NH_2 group lies in the plane of the ring but shows a significant distortion of the bond angles O—C—N and N—C—N [116·3 (2) and 129·0 (1)°] that may be due to non-bonding interactions.

The packing distances are in the range 3·60–4·20 Å. Several MO calculations have been carried out for oxazole and it may be interesting to compare the calculated geometry for this molecule (Roche, D'Amato & Benard, 1971) with that found for the present compound (*cf.* Table 2).

There is good overall agreement between the calculated values for oxazoles and the geometry found here, it being possible to ascribe the differences to the presence of the NH_2 substituent.

References

Albinati, A. & Brückner, S. (1978). *Acta Cryst.* B**34**, 3390–3392.

Allman, R. (1975). *The Chemistry of the Hydrazo, Azo and Azoxy Groups*, edited by S. Patai, pp. 23–52. New York: John Wiley.

Ambats, I. & Marsh, R. E. (1965). *Acta Cryst.* **19**, 942–948.

Bovio, B. & Locchi, S. (1972). *Cryst. Struct. Commun.* **1**, 253–256.

Cruickshank, D. W. J. (1970). *Crystallographic Computing*, edited by F. R. Ahmed, pp. 187–197. Copenhagen: Munksgaard.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Kálmán, A., van Meurs, F. & Toth, J. (1980). *Cryst. Struct. Commun.* **9**, 709–712.

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[*] Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP36163 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

La Cour, T. & Rasmussen, S. E. (1973). *Acta Chem. Scand.* **27**, 1845–1850.
Lakhan, R. & Ternai, B. (1974). *Adv. Heterocycl. Chem.* **17**, 99–211.
Levsen, K. (1978). *Fundamental Aspects of Organic Mass Spectrometry.* Weinheim: Verlag Chemie.
Main, P., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1974). *MULTAN 74. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.
Roche, M., D'Amato, F. & Benard, M. (1971). *J. Mol. Struct.* **9**, 183–189.
Selva, A., Traldi, P., Rapi, G., Ginanneschi, M. & Chelli, M. (1979). *Org. Mass Spectrom.* **14**, 663–667.
Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions.* Spec. Publ. No. 18. London: The Chemical Society.
Traldi, P., Vettori, U. & Clerici, A. (1980). *Heterocycles*, **14**, 847–865.

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Structure of Alnusenone (*D*:*B*-Friedoolean-5-en-3-one)

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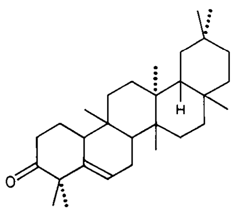
Abstract. $C_{30}H_{48}O$, M_r = 424·71, triclinic, *P*1, *a* = 7·338 (1), *b* = 14·856 (1), *c* = 6·267 (1) Å, α = 97·10 (1), β = 113·60 (1), γ = 93·20 (1)°, *Z* = 1, D_x = 1·10 Mg m^{-3}, μ(Cu *K*α) = 4·9 cm^{-1}. The structure was refined by a block-diagonal least-squares method. The final *R* value was 0·037 for 1904 reflexions. The *cis* fusion at the *D*/*E* junction and the axial α-methyl group at C(13) cause the *D* and *E* rings to be in the twist-boat and boat conformations respectively.

Introduction. Alnusenone (*D*:*B*-friedoolean-5-en-3-one, I), a naturally occurring triterpene (Chapon & David, 1953), was isolated from *Trogopterum Faeces* (Akamatsu, 1970).



(I)

Prismatic crystals were obtained from an acetone–methanol solution at room temperature. Oscillation and Weissenberg photographs indicated the crystal to be triclinic. As the compound is optically active, the space group should be *P*1. A crystal, 0·4 × 0·5 × 0·65 mm, was mounted on a Rigaku automated four-circle diffractometer. The unit-cell dimensions were determined by least-squares refinement of 2θ values for 22 high-angle reflexions.

Intensity data were collected on the diffractometer by the use of Ni-filtered Cu *K*α radiation (λ = 1·54184 Å), with an $\omega/2\theta$ scanning technique ($2\theta \le$ 122°). Five reference reflexions showed no significant intensity deterioration during the course of data collection. Corrections were made for Lorentz and polarization factors, but not for absorption. A total of 1904 independent reflexions were obtained, of which 7 reflexions had zero intensities [$I \le \sigma(I)$]. The standard deviations were estimated by the equation $\sigma^2(F_o) = \sigma_P^2(F_o) + qF_o^2$; here $\sigma_P(F_o)$ was evaluated by counting statistics and *q* (1·689 × 10^{-5}) was derived from the variations of the monitored reflexions.

Many peaks corresponding to cyclohexane rings appeared on an *E* map calculated with *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). One of the least-squares trials among several possible models gave a promising low *R* value,

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